EQUATION OF STATE FOR C_{60} FULLERENE AQUEOUS SOLUTION[1]

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ABSTRACT

In the present work the PVT data of the C_{60} fullerene aqueous solution (C_{60}FAS) were measured depending on the concentration of C_{60} molecules using the variable cell method with metal bellows in the temperature range from 295 to 360 K and pressure range from 0.1 to 103.2 MPa. Note that on the liquid-vapor equilibrium line the density (ρ) of the C_{60}FAS was measured using the picnometer method. As a result, we have found the numerical values for the isothermal modulus of elasticity (K_T), isobaric expansivity (α_P), isothermal deviation of entropy factor ($T\Delta S$), enthalpy (ΔH), and internal energy (ΔU). Finally, the equation of state for the C_{60}FAS was obtained for the first time.

KEY WORDS: fullerene aqueous solution, high pressures, equation of state

1. INTRODUCTION

Fullerenes are currently being widely investigated and have potential for various technical applications [1]. In particular, for biomedical testing, water-soluble forms of fullerenes are of great interest. It is known that fullerenes are allotropic form of carbon that consists of polyhedral sphere-like molecules with number of carbon atoms from 60 to 240. Exotic structure of fullerenes makes for their unusual behaviour in solutions [2-8]. In particular, the C_{60} fullerene aqueous solution (C_{60}FAS) is shown to be the ultramicroheterogeneous and polydisperse system containing spherical C_{60} aggregates (both single fullerene C_{60} molecules and their fractal clusters, with diameter from 7 to 36 nm) in a hydrated state (i.e., the fullerene aggregates are covered by a strong hydrated shell) [4-5]. The indirect optical transitions revealed also unequivocally prove the existence of the crystalline state of fullerene molecules as C_{60} fullerene aggregates in the water [8]. Hence, more detailed experimental and theoretical studies of the structure and thermophysical properties of the C_{60}FAS are important.

In this paper we present the results of studies of thermodynamic properties of the C_{60}FAS with C_{60} concentration equal to X_1 = 0.05 mg/ml, X_2 = 0.10 mg/ml, X_3 = 0.18 mg/ml and X_4 = 0.28 mg/ml.

2. EXPERIMENTAL

PVT measurements for the C_{60}FAS were carried out in the range of pressures from 0.1 to 103.2 MPa and in the range of temperatures from 295 to 360 K by variable cell method with metal bellows and differential inductive sensor of linear shifts [6-9]. Pressure measurement error was equal to 0.05% of actual measured value. Density and temperature measurement errors were less than 0.1%. Density of pure water was found in the review [10].

3. RESULTS

Thermobaric dependence of density ρ (kg/m^3) of investigated solutions is given in Table I and Fig. 1. As one can see the addition of fullerene C_{60} into water results in a shallow density growth at normal pressure. But when pressure increases the density curves for investigated solutions reveal lower steepness as compared to pure water. Higher concentrations of C_{60}FAS correspond to lower steepness of density curves. This fact indicates on the decrease of compressibility of the C_{60}FAS with the increase of concentration.

Thermodynamic properties such as isothermal elastic modulus K_T, isobaric expansivity α_P, entropy factor $T\Delta S$, enthalpy ΔH, and total internal energy ΔU were calculated according to the general thermodynamic formulas [11]:

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P,$$

$$K_T = -V\left(\frac{\partial P}{\partial V}\right)_T,$$

$$T\Delta S = -T \int_{P_0}^{P} \left(\frac{\partial V}{\partial T}\right)_P dP,$$

$$\Delta U = -T \int_{P_0}^{P} \left(\frac{\partial V}{\partial T}\right)_P dP - \int_{V_0}^{V} P dV,$$

$$\Delta H = \int_{P_0}^{P} \left(V - T\left(\frac{\partial V}{\partial T}\right)_P\right) dP.$$

The obtained results for some isotherms are presented in Fig. 2–6. As follows from Fig. 2, 3 isobaric expansivity α_P in solutions decreases, and isothermal elastic modulus K_T increases with the increase of concentration. Consequently, one can conceive that the energy of molecular interaction in the investigated solutions is increasing function of concentration. The isothermal deviation of entropy factor $T\Delta S$ (see Fig. 4) and the total internal energy ΔU (see Fig. 5) are of the same relative character. Deviation of these properties is higher for the solutions than for pure water. When the pressure increases the absolute values of all these isothermal deviations increase too. The isothermal deviation of enthalpy ΔH (see Fig. 6) is higher in solutions than in pure water. The increase of ΔH with the addition of fullerene C_{60} into water is not so great as in the case of entropy factor $T\Delta S$ and the total internal energy ΔU. Thus, we can conclude that the increase of internal energy is defined by its entropy term.

In order to describe the pressure dependence of thermodynamic properties for the C_{60} FAS analytically, we used the following simple empiric isothermal equations of state with a few parameters admitting statistical substantiation [12]:

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{A'}{B+P} \quad - \text{Tait}, \tag{1}$$

$$\ln \frac{PV^{2/3}}{V_0^{1/3} - V^{1/3}} = A_0 + B_0(V_0^{1/3} - V^{1/3}) \quad - \text{Hudleston}, \tag{2}$$

$$\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{A^*}{B^* + P} \quad - \text{Murnaghan}, \tag{3}$$

$$P = \frac{a}{V^2} + \frac{b}{V^9} \quad - \text{Ahoondov-Mamedov}, \tag{4}$$

$$P = \frac{a^*}{V^3} + \frac{b^*}{V^7} \quad - \text{Goloobev-Gooseinov}, \tag{5}$$

$$P = \frac{B'}{V - A'} + C' \quad - \text{Biron-Mamedov}. \tag{6}$$

In order to decide which of equations (1)–(6) should be preferred, all of them were rearranged to the form containing the same quantities defined in experiment [12]: P_0 is the reference (normal) pressure, ρ_0 is the reference density, $K_{T,0}$ is the elastic modulus in the reference state and $\left.\dfrac{\partial K_T}{\partial P}\right|_{T,0}$ its derivative. Experimental values of

$(P - P_0)/K_{T,0}$ were fitted according to the mentioned above equations of state. A qualitative agreement between equations (1)–(6) and experiment was tested by χ^2-criterion [13] (see Table II). As one can see in Table II all these equations are indistinguishable and describe experiment equally well up to pressures 50 MPa. They only deviate from experiment at higher pressures. Better fit of experimental $(P - P_0)/K_{T,0}$ versus P dependence is given by Tait (1), Hudleston (2) and Murnaghan (3) equations of state. In order to choose the most adequate of these three equations, we have plotted isothermal derivative $\left(\frac{\partial P}{\partial V}\right)_T$ as a function of pressure (see Fig. 7). It was found to be linear with random mean-square deviation (RMSD) less than 0.8% for all C_{60}FAS investigated. As follows from the analytic form of equations (1)–(6), the only equation of state leading to the linear character of $\left(\frac{\partial P}{\partial V}\right)_T$ versus P dependence is Tait one. Thus, it was accepted as the most adequate of them.

The integral form of Tait equation (1) is following

$$V = V_0 \left(1 - A \ln \frac{B + P}{B + P_0} \right), \tag{7}$$

$$P = (B + P_0) \exp \frac{V_0 - V}{A \cdot V_0} - B, \tag{8}$$

where V_0 is the molar volume in the reference state, $A = A'/V_0$ and B are the parameters of the equation of state.

We have calculated A and B parameters for Tait equation (7) (see Table III). The confidence intervals δA and δB were accordingly equal to 0.009 and 9 MPa with confidence probability equal to 95%. Parameter B as a function of temperature is presented in Fig. 8 for all investigated solutions and pure water. As one can see in Table III A and B values increase with the C_{60} concentration in water.

According to the statistic substantiation of Tait equation of state [14], parameter A is associated with repulsive potential steepness, and parameter B is associated with the energy of molecular attraction. Parameter A decreases with the increase of repulsive potential steepness and parameter B increases with the increase of energy of molecular attraction. Thus, taking into account the value of parameter A, we can conclude that repulsive potential steepness for pure water is higher than for the investigated solutions. At the same time, molecular attraction energy increases with addition of fullerene C_{60} into water over the whole investigated range of pressures, temperatures and concentrations. The last conclusion is in a full agreement to our previous assumption about molecular interaction energy.

Relying on the obtained A and B values we have calculated isobaric expansivity α_P, isothermal elastic modulus K_T, isothermal deviations $T\Delta S$, ΔH, and ΔU for the investigated C_{60}FAS.

Thermobaric dependencies of α_P and K_T are described with RMSD accordingly equal to 2% and 1%. Thermobaric dependencies of isothermal deviations $T\Delta S$, ΔH, and ΔU are described with RMSD equal to 2%, 2% and 2.5%, respectively. The experimental and calculated values of the isothermal deviation of enthalpy as function of pressure for the C_{60}FAS are represented in Fig. 9.

4. CONCLUSIONS

The following conclusions can be reached:

1. *PVT* data for the C_{60}FAS is described by Tait equation of state (7) over the whole investigated range of pressures and temperatures with parameter *A* as a function of concentration and parameter *B* as a function of temperature and concentration. The obtained equation adequately describes thermobaric dependencies of investigated thermodynamic properties over the whole investigated range of pressures and temperatures.

2. From the analysis of thermodynamic properties follows that the energy of molecular attraction in the investigated solutions is increasing function of concentration over the investigated range of pressures and temperatures.

3. Isothermal equilibrium growth of pressure in the C_{60}FAS leads to the same relative character of isothermal deviations $T\Delta S$, ΔH and ΔU: the deviation values increase with the increase of C_{60} concentration in water.

4. The increase of the energy of molecular interaction in the investigated solutions is due to entropy changes of aqueous system.

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Table I. Thermobaric dependence of density ρ (kg m^{-3}) for the C_{60} FAS

X (mg/ml)	P (MPa)	T (K)			
		295	319	342	360
0.05	0.1	998	991	979	969
	7.0	1001	993	982	972
	49.2	1019	1010	999	989
	103.2	1039	1030	1018	1008
0.10	0.1	999	991	980	970
	7.0	1002	994	982	973
	49.2	1019	1010	998	989
	103.2	1038	1028	1017	1008
0.18	0.1	999	992	982	972
	7.0	1002	994	984	974
	49.2	1017	1009	998	989
	103.2	1037	1027	1016	1007
0.28	0.1	1001	994	984	974
	7.0	1003	996	985	976
	49.2	1017	1009	998	989
	103.2	1035	1025	1014	1005

Table II. Some $(P - P_0)/K_{T,0}$ values for the C_{60} FAS with concentration X_4 at 360 K

P (MPa)	$(P - P_0)/K_{T,0}$						
	Exper.	(1)	(2)	(3)	(4)	(5)	(6)
0.1	0	0	0	0	0	0	0
0.5	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002
10.8	0.0049	0.0049	0.0049	0.0049	0.0049	0.0049	0.0049
23.6	0.0108	0.0108	0.0108	0.0108	0.0108	0.0108	0.0108
51.5	0.0236	0.0236	0.0236	0.0236	0.0236	0.0236	0.0236
66.8	0.0306	0.0306	0.0306	0.0306	0.0307	0.0307	0.0306
86.6	0.0397	0.0397	0.0398	0.0397	0.0398	0.0399	0.0397
103.2	0.0474	0.0473	0.0474	0.0474	0.0474	0.0476	0.0472
χ^2		0.001	0.001	0.001	0.002	0.017	0.003
RMSD (%)		0.5	0.4	0.4	0.8	2.2	1.0

Table III. Calculated A and B parameters of Tait equation of state (1) for pure water and C_{60} FAS with different concentrations

T (K)	295	319	342	360
		H_2O		
A		0.137		
B (MPa)	296	308	303	293
		X_1		
A		0.146		
B (MPa)	351	361	358	348
		X_2		
A		0.196		
B (MPa)	460	484	480	465
		X_3		
A		0.198		
B (MPa)	525	552	553	538
		X_4		
A		0.292		
B (MPa)	867	936	942	927

Figure Captions

Fig. 1. Themobaric dependence of density ρ (kg m^{-3}) at 319 and 360 K.

Fig. 2. Isobaric expansivity α_P at 319 and 360 K.

Fig. 3. Isothermal elastic modulus K_T at 319 and 360 K.

Fig. 4. Isothermal deviation of entropy factor $T\Delta S$ at 319 and 360 K.

Fig. 5. Isothermal deviation of total internal energy ΔU at 319 and 360 K.

Fig. 6. Isothermal deviation of enthalpy ΔH at 319 and 360 K.

Fig. 7. Thermobaric dependence of isothermal derivative $\left(\frac{\partial P}{\partial V}\right)_T$ at 319 and 360 K.

Fig. 8. Tait parameter B as a function of temperature for the C_{60}FAS and pure water.

Fig. 9. Isothermal deviation of enthalpy as a function of pressure for the C_{60}FAS at concentration X_4 and $T = 360$ K.